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TITLE: DETERMINATION OF CHLORINATED BENZENES IN SOIL AND SEDIMENT

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ABSTRACT: The chlorobenzenes are extracted from the soil/sediment sample with an organic solvent using the procedure described in Standard Operating Procedure (SOP) EAN-80-SOP-20, Extraction of Semivolatile Organic Chemicals from Soil/Sediment. The chlorobenzenes in the extract are measured by selected ion monitoring (SIM) gas chromatography/mass spectrometry (GC/MS) and quantitated using external standards. The recovery and precision levels determined during method validation varied depending on compound and concentration.

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R-1088(B)
R-1088(A)

DETERMINATION OF CHLORINATED BENZENES IN SOIL AND SEDIMENT

1. SCOPE

1.1 This method is for the determination of chlorinated benzenes in soil and sediment samples.

1.2 The method is applicable to samples containing 1 μg/g to 50 μg/g (ppm) of any individual chlorobenzene. Higher levels can be determined by diluting sample extracts or by analyzing smaller samples. However, proper validation at these higher levels should be carried out.

1.3 The method has been validated using a Missouri Bottoms soil sample. Proper quality assurance must be carried out to verify the performance of the method for other soils and sediments.

1.4 The method validation was done using benzene as the extraction solvent, because of a specific application of the method. In normal applications, isooctane is the recommended solvent. However, proper quality assurance must be carried out to verify the satisfactory performance of this solvent.

1.5 This method has been fully validated for mono-, di-, and trichlorobenzenes and nitrochlorobenzenes. However, with proper quality assurance, it is also applicable to tetra-, penta-, and hexachlorobenzenes.

2. SUMMARY

2.1 The chlorobenzenes are extracted from the soil/sediment sample with an organic solvent using the procedure described in Standard Operating Procedure (SOP) EAN-80-SOP-20, Extraction of Semivolatile Organic Chemicals from Soil/Sediment.

2.2 The chlorobenzenes in the extract are measured by selected ion monitoring (SIM) gas chromatography/mass spectrometry (GC/MS) and quantitated using external standards.

2.3 The recovery and precision levels determined during method validation varied depending on compound and concentration.

3. SIGNIFICANCE

3.1 Chlorobenzenes are widely used industrial chemicals and may also occur as contaminants of industrial processes. As such, the potential exists for the chemicals to be present in industrial wastes.

3.2 This method provides a technique to measure chlorobenzenes in samples from sites potentially contaminated by the disposal of such wastes.

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4. INTERFERENCES

4.1 Although the SIM GC/MS is a very sensitive and selective detector for the determination of the chlorobenzenes, the potential exists for mass spectral interferences at one or more of the ions used for the determinations.

4.2 Use of ion intensity ratio comparisons for the molecular weight ion and a confirming ion can help identify such interferences.

4.3 All sampling equipment (if used), solvents, and laboratory glassware must be demonstrated to be free of interferents by the analysis of field and laboratory blanks.

5. SAFETY PRECAUTIONS

5.1 Benzene is a suspected human carcinogen. Extreme care must be taken when preparing standards or extracting samples. Use of a personal exposure monitoring system may be required. Avoid use of benzene if possible.

5.2 HCB is a suspected carcinogen. Extreme care must be taken when preparing standards from neat materials. Avoid all contact with standards and samples.

5.3 Sediment or soil samples may contain pathogens. They should be handled as little as possible and then only by persons who have a current innoculation against typhoid.

5.4 All GC/MS vacuum pumps, especially the separator pump, must be equipped with a charcoal scrubber or must discharge into a scrubbed ventilation system to prevent discharge of hazardous vapors into the laboratory atmosphere.

6. APPARATUS

6.1 Apparatus required for EAN-80-SOP-20

6.1.1 Ultrasonic homogenizer - Polytron® (Brinkmann Instruments) or equivalent.

6.1.2 Test tubes - polypropylene, 50 mL

6.1.3 Centrifuge - refrigerated, capable of 15,000 rpm

6.1.4 Receivers - graduated 10 mL Kuderna-Danish receivers.

6.2 GC/MS - equipped with data system for instrument control and data accumulation and retrieval; must be capable of SIM operation and equipped for subambient gas chromatography.

6.3 Glass column for gas chromatograph - 1 m x 2 mm i.d., packed with a suitable packing (See Sec. 7.1).

6.4 Microsyringe - 10 µL capacity.

6.5 Usual laboratory volumetric glassware.

7. REAGENTS AND MATERIALS

7.1 GC column packing - 3% OV-101 on 100/120 mesh Gas Chrom® Q has been found suitable and was used for validation studies.

7.2 Benzene - Fisher Scientific Company - Pesticide Grade or equivalent. Benzene must be demonstrated to be free of analyte.

7.3 Isooctane - Burdick & Jackson - "Distilled in glass" or equivalent.

7.4 Chlorobenzene samples - characterized neat materials.

7.5 Stock standards - Prepare a stock standard solution (∿1000 µg/mL) of each chlorobenzene of interest by weighing 0.1g (to the nearest mg) of each material into a separate 100 mL volumetric flask and diluting to volume with the extraction solvent.

7.6 Working standards - Prepare mixed working standards in the concentration range of interest by combination and subsequent successive dilution of the stock standards. At least three working standards must be prepared, with concentration ranges not to exceed one decade.

8. SAMPLING

8.1 Soil or sediment samples should be collected according to established procedures, using clean equipment.

8.2 Label each sample container with its corresponding sample number and history.

8.3 A number of sampling blanks equal to at least 10% of the total number of samples should be collected at the sampling site.

8.4 In the laboratory, samples should be handled in accordance with EAN-80-SOP-006, SOP for Homogenizing, Subdividing, and Preserving Sediment Samples.

8.5 At least 10% of the samples should be analyzed in triplicate to determine precision.

8.6 At least 10% of the samples should be spiked at appropriate levels (e.g., 2X, 10X or 100X the estimated level in the samples) to determine accuracy (recovery).

9. CALIBRATION AND STANDARDIZATION

9.1 Mass spectometer calibration

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9.1.1 The sensitivity and mass offset (if applicable) of the mass spectrometer should be checked on a daily basis using a suitable calibration material, e.g., perfluoro-t-butyl amine ((PFTBA).

9.1.2 Record the calibration results in the calibration log for the instrument.

9.2 Reference Standards and Blanks

9.2.1 GC retention times for each chlorobenzene of interest should be determined by injecting 1 µL of each stock standard into the GC/MS operating in the scanning mode. The retention data and mass spectra are used to select SIM conditions (selected ions and mass group retention windows) for the determinations.

9.2.2 Field blanks (Section 8.5) and laboratory blanks (Section 4.3) (at least one per day) should be analyzed according to the procedure (Section 10).

9.3 Calibration Curves or Response Factors

9.3.1 The linearity of response for SIM GC/MS must be determined for each analyte. Inject equal volumes (e.g., 3 µL) of various concentrations of working standards and measure the area of each peak corresponding to an analyte of interest.

9.3.2 For initial calibration, at least 3 working standards and a solvent blank should be analyzed in triplicate.

9.3.3 For routine use, at least three working standards and a solvent blank should be analyzed in duplicate on a daily basis to determine linearity and response factors.

9.3.4 For each analyte, linearity can be established by plotting a calibration curve (peak area vs ng injected (or vs concentration if equal injection volumes are used)) or by calculating a response factor (RF) (ng injected or concentration ÷ peak area) and plotting RF vs ng injected or vs concentration. Only sample peak areas which fall in the linear response range should be used to calculate concentrations.

9.3.5 Computer programs which calculate RFs, average RFs and standard deviation (SD), and perform a least-squares analysis can also be used. In general, a $\pm$ 20% relative SD (RSD) and a least squares correlation coefficient (R) of >0.95 are acceptable indicators of linearity.

9.3.6 Table I contains the RF, RSD, and R for the calibration phase of method development.

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TABLE I

Compound	RF (ppm/area count)		RSD (%)	R
Cl_1 benzene	1.85	E-4	14	.993
p-Cl_2 benzene	3.22	E-4	17	.99
o-Cl_2 benzene	2.64	E-4	23	.991
1,3,5-Cl_3 benzene	2.64	E-4	12	.992
o-Nitrochlorobenzene	9.43	E-4	10	.99
Cl_6 benzene	2.78	E-4	15	.994

10. PROCEDURE

10.1 Extraction

10.1.1 Extract the chlorobenzenes from the soil or sediment samples using the procedure described in EAN-80-SOP-20, Extraction of Semivolatile Organic Chemicals from Soil/Sediment.

10.1.2 Extract the number of replicates and spiked samples necessary to comply with quality assurance requirements (see Section 8.5 and 8.6).

10.1.3 Store extracts in a refrigerator if they are not analyzed immediately.

10.2 SIM GC/MS Analysis

10.2.1 Operate the GC/MS according to Standard Operating Procedure or manufacturer's instructions.

10.2.2 The following conditions have been found suitable for the chromatography of chlorobenzenes.

Column: 1 m x 2 mm i.d. glass column packed with 3% OV 101 on 100/120 mesh Gas Chrom Q.

Column Temperature: Program from 10°C to 200°C @ 16°C/min

Carrier Gas: Helium, 30 mL/min

Injection Port Temperature: 250°C

Jet Separator Manifold Temperature: 300°C

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10.2.3 The following conditions have been found suitable for the SIM GC/MS determinations using an HP 5982A GC/MS system with associated 5934A data system:

Ion Source Temperature: 150°C
Separator: Glass jet
Ionization: Electron impact - 70 eV or equivalent
Electron Multiplier Gain: 9 or 10 HI
Selected Ion Dwell Times: 200 ms

10.2.4 The selected ions, dwell times, and retention window groups are shown in Table II. Note that exact group starting times will be affected by anything that influences retention, such as column packing, column conditions, carrier flow, etc., so that the start times will have to be determined for any new set of conditions.

10.2.4 If the samples have been frozen for storage, allow to equilibrate to room temperature.

10.2.6 Inject a suitable size aliquot of the sample into the GC/MS. (If the injection volume equals that of the calibration standards, calculations are simplified.)

10.2.7 Measure peak areas for the peaks at the retention times or within retention windows for the compounds of interest. Check ion intensity ratios for molecular and confirming ions to be sure that interferences are not present.

10.2.8 Sample SIM chromatograms for a mixed chlorobenzene standard are shown in Figure I A-D. (Figure I B includes ions for phosphorus, which just happened to be a co-analyte for these samples.)

11. <u>CALCULATION OF RESULTS</u>

11.1 If injection volumes are not all equal:

11.1.1 Calculate the mass of each analyte by comparing to a calibration curve prepared daily or by calculating from the response factor using the equation:

$$Mi = (RFi)(Ai)$$

where:

Mi = mass of analyte injected (ng)

RFi = response factor for analyte (ng/area count)

Ai = peak area for analyte (area counts)

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11.1.2 Calculate the concentration of each analyte using the following equation:

$$Ci = \frac{(Mi)(V_F)(DF)}{(V_I)(W)}$$

where:

Ci = concentration of analyte (μg/g = ppm)

Mi = mass of analyte (from Section 11.1.1)

V_F = volume of extract (mL)

V_I = injection volume (μL)

W = sample weight (g)

DF = dilution factor (Section 10.2.9)

11.2 If injection volumes are equal (e.g., 3 μL):

11.2.1 Calculate the concentration of each analyte by comparing to a calibration curve prepared daily or by calculating from the response factor using the equation:

$$Ci = \frac{(RFi)(Ai)(V_F)(DF)}{W}$$

where:

Ci = concentration of analyte (μg/g = ppm)

RFi = response factor for analyte (ppm/area count)

Ai = peak area for analyte (area counts)

V_F = volume of extract (mL)

DF = dilution factor (Section 10.2.9)

W = sample weight (g)

12. <u>REPORT</u>

12.1 Report the results in μg/g (or ppm) without correction for recovery.

12.2 Report recoveries and precision determined on spiked samples and replicates.

12.3 Report results for all sampling and laboratory blanks.

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13. PRECISION AND ACCURACY

13.1 The precision and accuracy of this method were determined in a soil matrix (Missouri Bottoms) at four levels by analysis of five replicates at each spiking level plus blanks.

13.2 The precision and accuracy results are summarized in Table III. The recoveries are averages of all replicates at each spiking level. The precision is reported as relative standard deviation.

14. REFERENCES

14.1 The raw data for this method validation is found in Monsanto Research Notebook pages:

OH 1805238-9
RGK 1914813-5, 1914823

TABLE II

SELECTED IONS AND DWELL TIMES

GROUP I

Start Time = .0

Mass	Dwell Time (ms)	
112.0	200	Cl_1 Benzene
114.0	200	

GROUP II

Start Time = 3.0

Mass	Dwell Time (ms)	
93.0	200	
111.0	200	(Phosphorus)
124.0	200	Cl_2 Benzene
146.0	200	

GROUP III

Start Time = 4.3

Mass	Dwell Time (ms)	
111.0	200	
145.0	200	NCBs
157.0	200	Cl_3 Benzene
180.0	200	

GROUP IV

Start Time = 6.2

Mass	Dwell Time (ms)	
111.0	200	NCBs
157.0	200	
179.0	200	Cl_4 Benzene
214.0	200	

GROUP V

Start Time = 7.7

Mass	Dwell Time (ms)	
248.0	200	Cl_5 Benzene
250.0	200	
282.0	200	
284.0	200	Cl_6 Benzene

NOTE: Groups I and II can be combined if phosphorus is excluded.

TABLE III

RECOVERY AND PRECISION RESULTS

Cl_1 Benzene			p-Cl_2 Benzene			o-Cl_2 Benzene			1,3,5-Cl_3 Benzene			o,p-Nitrochlorobenzene		
Level (ppm)	Recovery (%)	RSD (%)	Level (ppm)	Recovery (%)	RSD (%)	Level (ppm)	Recovery (%)	RSD (%)	Level (ppm)	Recovery (%)	RSD (%)	Level (ppm)	Recovery** (%)	RSD (%)
1	91	13	1	120	10	1	130	5	1	120	12	2.0	140	10
5	38	87	5	80	28	5	81	23	5	100	13	10	140	10
10	13	11	10	58	9	10	57	7	10	82	10	20	130	4
50	56	25	50	93	10	50	90	10	50	100	13	100	120	12
5	98	11	5	150	7	5	130	2						
10	69	13	10	110	9	10	100	10						
50	104	17	50	120	10	50	120	9						

** High recoveries may be a result of quantitating both o- and p-NCB with an o-NCB standard

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FIGURE I A

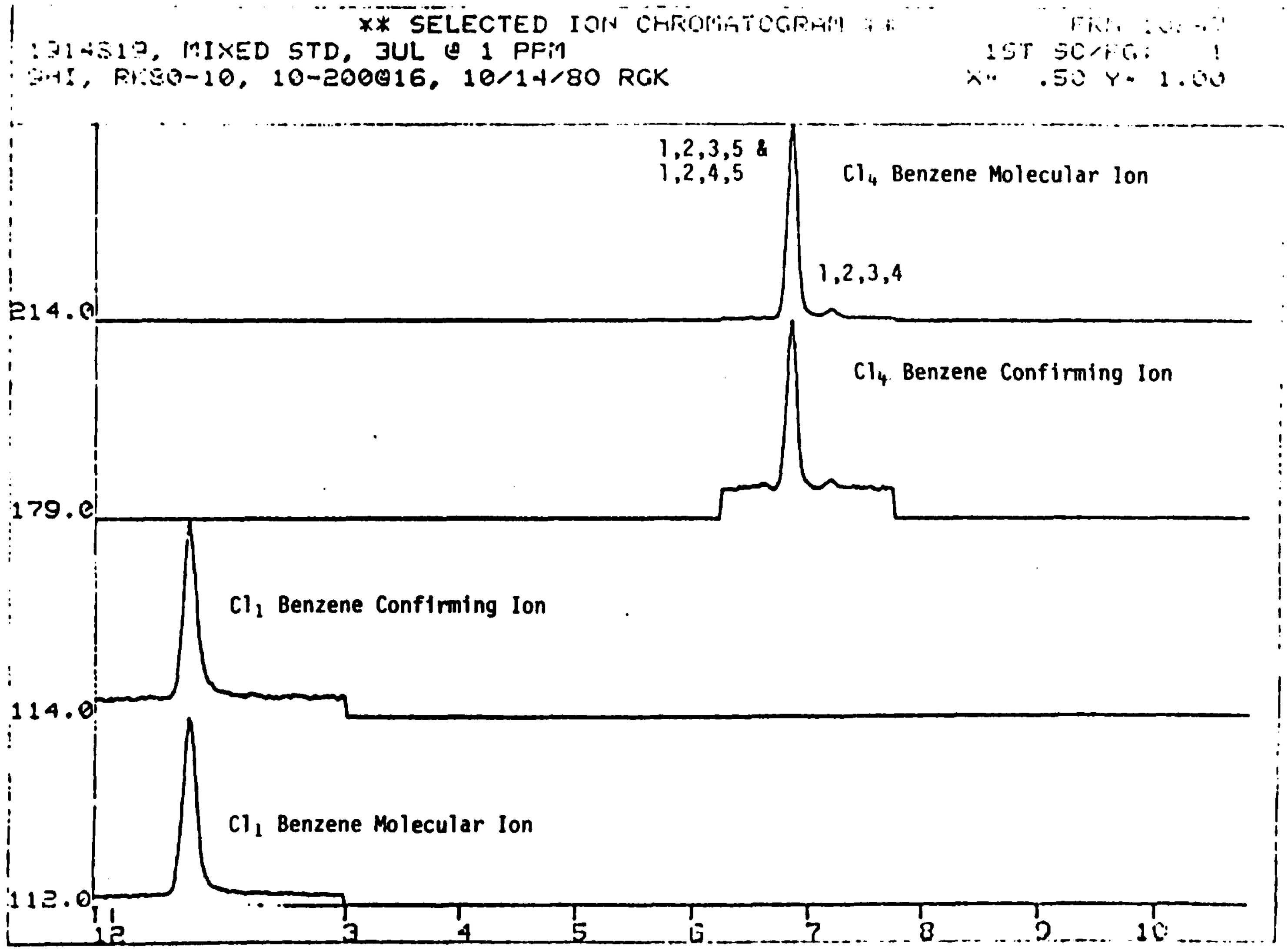

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FIGURE I B

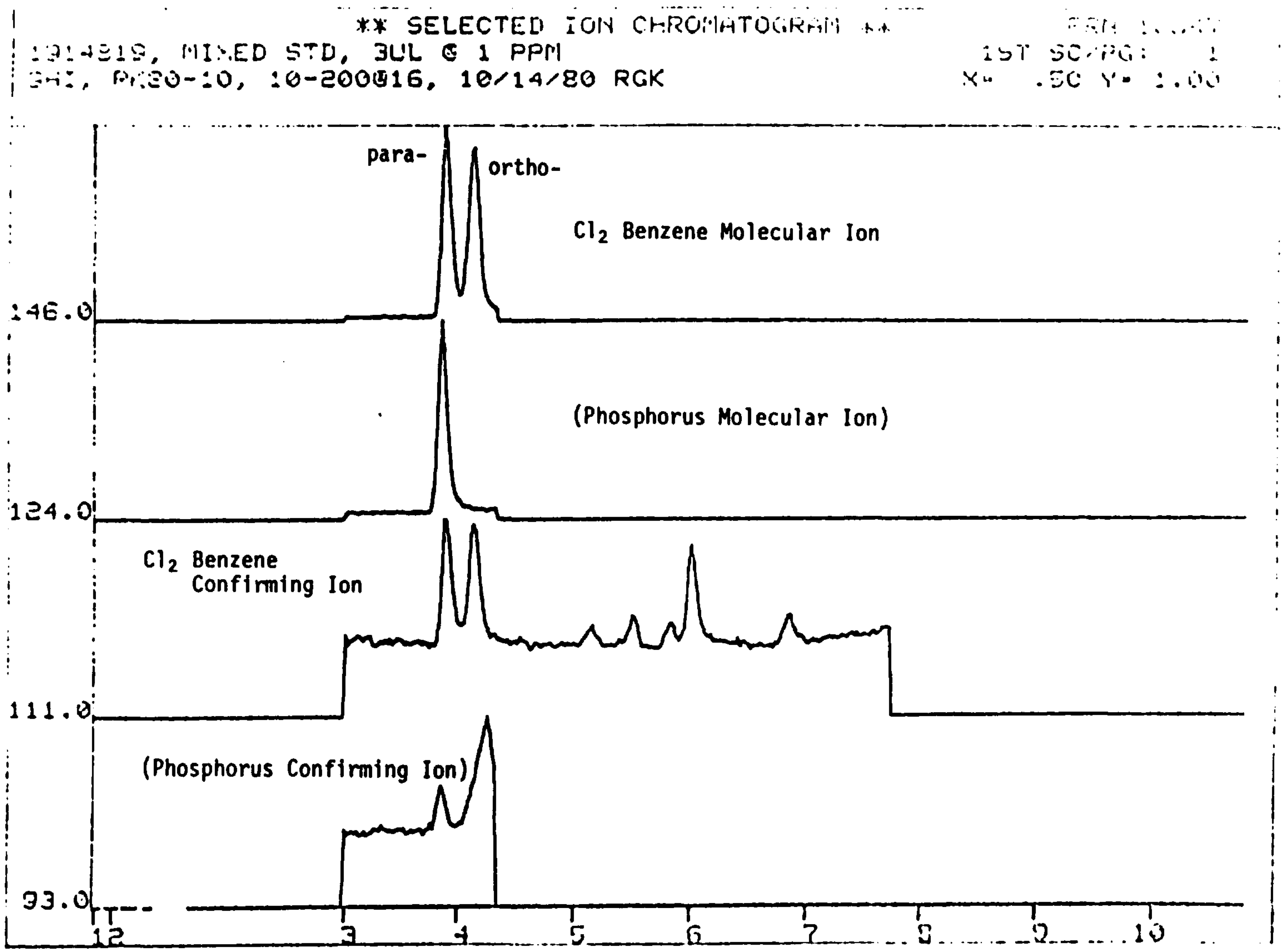

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FIGURE I C

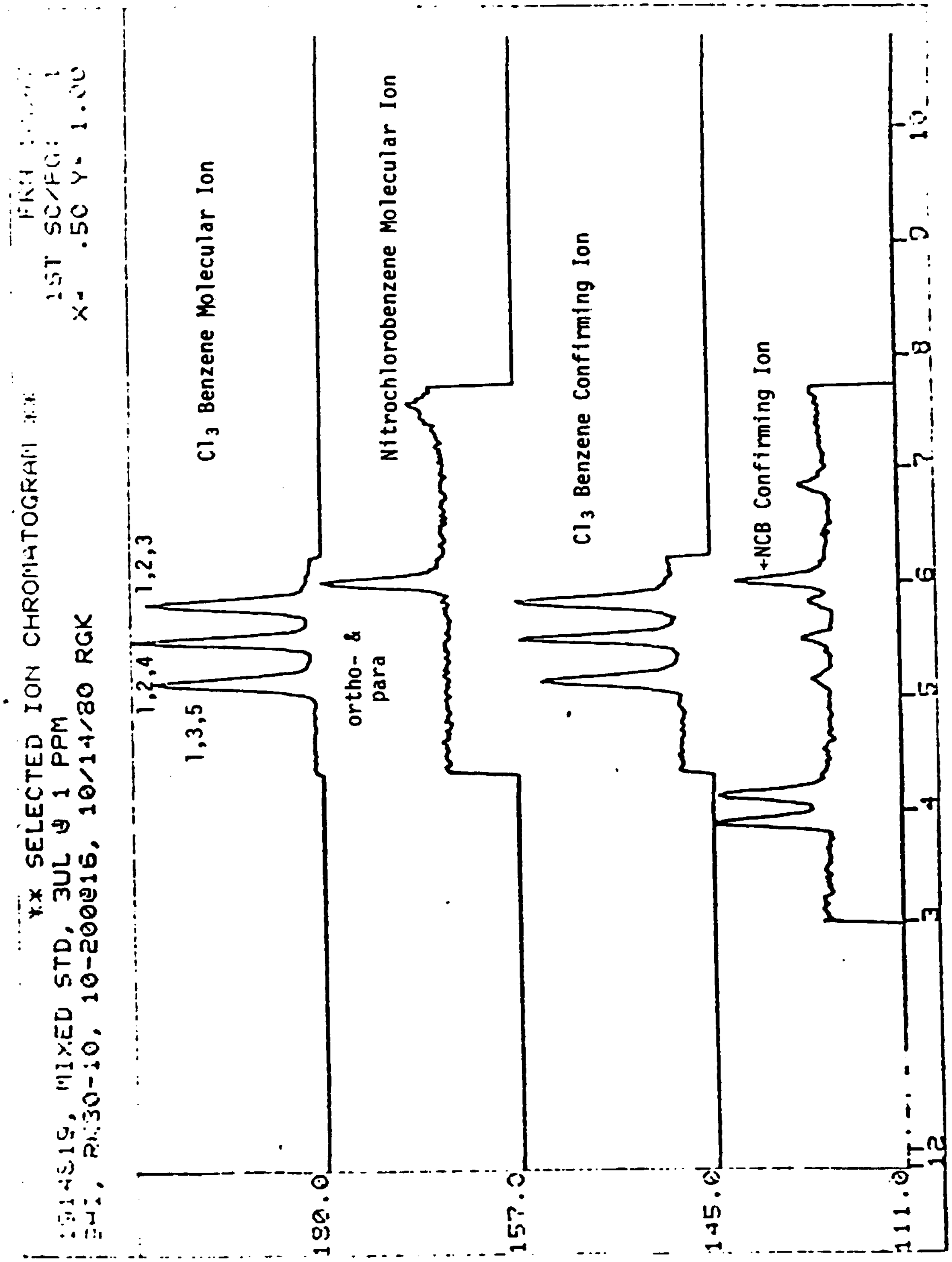

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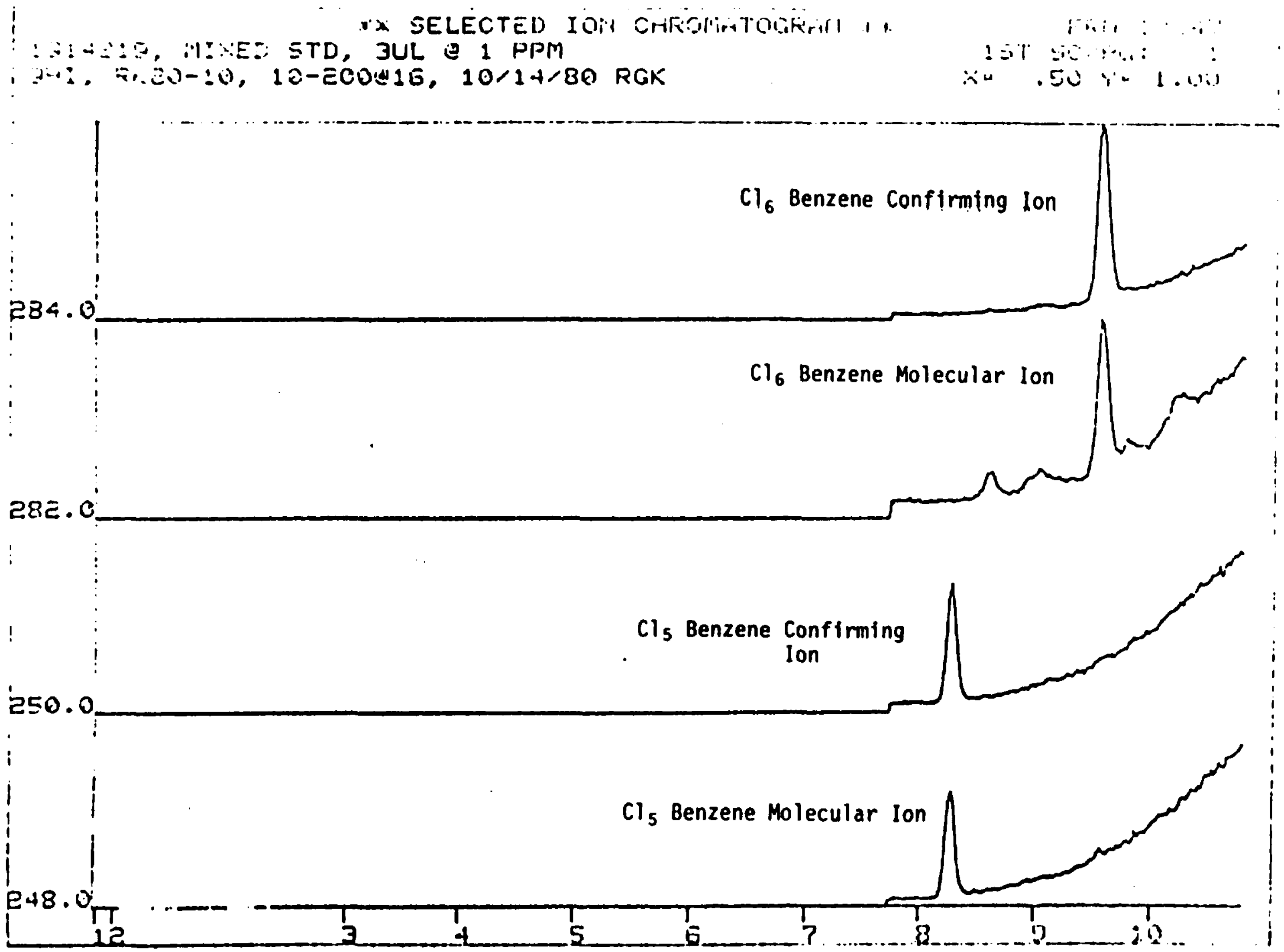
FIGURE I D



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